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Preliminary Note

Preliminary NMR Data of Ammonium Heptafluorozirconate

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Some time ago, Pauling and Hampson[1] investigated the room temperature crystal structure of ammonium heptafluorozirconate and found that the substance contained the ion $(ZrF_7)^{3-}$ and not $(ZrF_6)^{2-}$ and F^- ions as suggested earlier.[2] However, they were not able to assign all the atoms to definite positions in the unit cell and had to assume some disorder in the orientation of the ZrF_7 complexes. In an attempt to provide evidence for molecular disorder in this crystal as well as to determine whether the structure is statically or dynamically disordered, we undertook a proton and fluorine magnetic resonance study of polycrystalline $(NH_4)_3ZrF_7$ over the temperature range 80°—300° K.

The sample was prepared by adding 100% excess ammonium fluoride (as a 30% solution) to a solution of ZrO_2 in aqueous hydrofluoric acid, from which excess acid had been driven off by repeated dilution and heating.[3] The composition of the sample was confirmed from its chemical analysis and X-ray powder diagrams.

Over the whole temperature range investigated the ^{19}F magnetic resonance absorption spectra exhibit a single absorption peak with no fine structure. Its room temperature second moment of about 1.5 Gauss[2] indicates that the ZrF_7 ions rotate at this temperature. The room temperature structure should be thus dynamically rather than statically disordered. The occurrence of

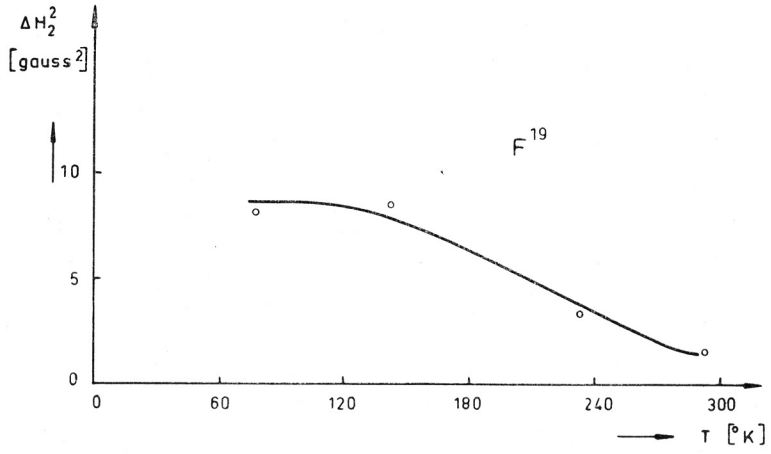

Fig. 1. Temperature dependence of ^{19}F NMR absorption second moment.

dynamical disorder and molecular reorientation at room temperature is directly confirmed by the temperature dependence of the ^{19}F magnetic resonance spectra (Fig. 1.). Between 290° and 100° K a broad, but distinct line width transition is found. Also the NH_4 group protons undergo an NMR line width transition in approximately the same temperature interval. The second moments of the proton spectra change from 3 Gauss^2 at room temperature to 33.5 Gauss^2 at 77° K. This observation suggests that the NH_4 groups reorient almost isotropically at room temperature. However, the fluorine and proton NMR data suggest dynamical disorder in the studied substance.

A more detailed report, including the Van Vleck sums for the Pauling model, and both fluorine and proton spin-lattice relaxation data, is being prepared.

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IZVLEČEK

Preliminarni NMR podatki o amonijevem heptafluorocirkonatu

Merjena je bila NMR absorpcija ^{19}F in H jeder v $(NH_4)_3ZrF_7$ v temperaturnem območju med 80 in 300° K. Majhna vrednost drugega momenta obeh magnetnih jeder pri sobni temperaturi dokazuje, da ioni ZrF_7 in NH_4 skoraj izotropno rotirajo pri tej temperaturi. Meritev potrjuje dinamični strukturni model.

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